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Request for grant of a patent

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21 JUN 1996

The Patent Office

Cardiff Road
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1. Your reference

BP-08-1054

2. Patent application number
(The Patent Office will fill in this part)

9613023.2

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

THE MORGAN CRUCIBLE COMPANY PLC
Morgan House, Madeira Walk,
Windsor
Berkshire
SL4 1EP

Patents ADP number *(if you know it)*

6283178001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

SALINE SOLUBLE INORGANIC FIBRES

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

PHILLIPS & LEIGH
7 Staple Inn
Holborn
London WC1V 7QF

Patents ADP number *(if you know it)*

0001289001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

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9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	–
Description	4
Claim(s)	1
Abstract	–
Drawing(s)	–

10. If you are also filing any of the following, state how many against each item.

Priority documents	–
Translations of priority documents	–
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	To follow
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	–
Any other documents *(please specify)*	–

11. I/We request the grant of a patent on the basis of this application.

Signature PHILLIPS & LEIGH Date 21.06.96

12. Name and daytime telephone number of person to contact in the United Kingdom J.C. BOFF 0171 405 0133

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DUPLICATE

SALINE SOLUBLE INORGANIC FIBRES

This invention relates to saline soluble inorganic fibres.

Saline soluble inorganic fibres have been described in several patent specifications, see for example WO93/15028. Fibres are required to be soluble in saline solution so that inhaled or ingested fibres dissolve rather than providing a source of irritation or otherwise affecting health. WO93/15028 showed that fibres comprising SiO_2, CaO and MgO and having a silica content of greater than 58% (or greater than 58% plus 0.5 times (10-MgO) if MgO > 10wt%) had suitable shrinkage characteristics at 800°C and 1000°C to be usable as refractory materials. A further feature of WO93/15028 was the use of the percentage of non-bridging oxygens present to predict the solubility of fibres in physiological saline solution.

Various subsequent applications have described the effect of P_2O_5 and B_2O_3 on solubility - see for example WO95/29135. P_2O_5 is alleged to have a solubilising effect on such fibres.

The German government have proposed a fibre classification which turns on a variable K_I which is defined as:

$$K_I = \Sigma(\text{ Na,K,B,Ca,Mg,Ba -oxide}) - 2^* \text{ Al-oxide}$$

(the amounts of the oxides being expressed as weight %)

According to the proposed fibre classification if K_I is greater than 40 the fibre concerned is deemed safe. If K_I lies between 30 and 40 the fibre requires only minor health warnings to be made. If K_I is less than 30 more serious marking is required. It is readily apparent that it is difficult to provide a high K_I fibre (K_I>40) while still providing a refractory fibre like that of WO93/15028 (SiO_2>58wt%), there being a very narrow window of compositions to meet.

As a result of investigating fibre compositions that may meet the fibre classification and yet still be refractory enough to meet the standard of WO93/15028 (shrinkage of less than 3.5% at both 800°C and1000°C) the applicants have found that addition of P_2O_5 to compositions allows a broader range of refractory fibres to be produced than had previously been appreciated.

It appears that an important factor in determining the refractoriness of a fibre is the percentage of non-bridging oxygens. If this percentage is 61.4% or more (calculated on the basis of the amounts of the components SiO_2 CaO, MgO,

P_2O_5, and B_2O_3) the fibres fail shrinkage tests at 800°C and 1000°C (failure being defined as a shrinkage of 3.5% or more).

Accordingly the present invention provides the use of P_2O_5 as a component to improve the refractoriness of inorganic fibres comprising SiO_2, and CaO and/or MgO, the inorganic fibres having a composition such that the percentage of non-bridging oxygens is less than 61.4%.

The invention further provides saline soluble inorganic fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, comprising:-

SiO_2	52 - <58wt% [52 - <58+0.5×(MgO-10)wt% if MgO > 10wt%]
CaO	22 - 40wt%
MgO	0 - 17.5wt%
MgO + CaO	< 42wt%
P_2O_5	0.5 - 10wt%
B_2O_3	0 - 2wt%

and in which the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is less than 61.4%.

The percentage of non-bridging oxygens (%N.B.O.) is calculated by converting the weight percentages of SiO_2 CaO, MgO, P_2O_5, and B_2O_3 to molar amounts and inserting these amounts into the equation:-

$$\%N.B.O.=\frac{2\times(CaO+MgO+P_2O_5+B_2O_3)}{(2\times SiO_2+CaO+MgO+5\times P_2O_5+3\times B_2O_3)}\times 100$$

The reason the amounts of CaO, MgO, P_2O_5, and B_2O_3 are doubled in the numerator to this equation is that each contributes two non-bridging oxygens. The reason terms are multiplied in the denominator to this equation is to reflect the number of oxygen atoms each molecular formula possesses.

Table 1 shows the results of shrinkage and solubility tests on compositions comprising SiO_2 CaO, MgO, P_2O_5, and B_2O_3 as main ingredients. It is clear that where the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is greater than 61.4% (those fibres lying above line A of Table 1) the fibres fail the shrinkage tests, having shrinkages of greater than 3.5% at either or both of 800°C and 1000°C.

WO93/15028 stressed the importance of alumina content and the fibres lying between lines B and A of Table 1 show that alumina contents of greater than 1wt% are damaging to the shrinkage properties of fibres.

The applicants have also found that the combined amount of CaO and MgO is important. Those fibres lying between lines C and B have a combined CaO and MgO content of greater than 42wt% and also fail the shrinkage tests.

The fibres below line C have a percentage of non-bridging oxygens less than 61.4%, an alumina content of less than 1wt%, and a combined CaO and MgO content of less than 42wt%. All of these fibres pass the shrinkage tests. These fibres fall within the compositional ranges:-

SiO_2	52.4 - 57.85wt%
CaO	22.2 - 39.4wt%
MgO	1.96 - 17.4wt%
P_2O_5	0.82 - 7.8wt%
B_2O_3	0 - 1.95wt%
Al_2O_3	<1wt%

The solubility results presented in Table 1 were obtained by the methods described in WO93/15028 and show a high solubility for all of the fibres produced.

It can be seen that all of the fibres below line C have a K_1 of more than 35 and more than half have a K_1 of more than 40.

While the above description and the claims refer to P_2O_5, B_2O_3, SiO_2, CaO and MgO it will be clear to the person skilled in the art that the pure materials need not be used and that provision of these components in combined form (e.g. provision of P_2O_5 in the form of mixed oxide phosphates) is part of the invention.

Code	Chemical Composition (XRF - Weight percent)											KI	Shrinkage		Solubility (ppm)						% N.B.O.	
LTP	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO		800°C	1000°C	CaO	MgO	SiO2	B2O3	Total	CaO+MgO		
Code	**Chemical Composition (XRF - Weight percent)**											**KI**	**Shrinkage**		**Solubility (ppm)**						% N.B.O.	
LTP	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO		800°C	1000°C	CaO	MgO	SiO2	B2O3	Total	CaO+MgO		
LTP 8	24.95	19.18	3.41	51.69	0.25	0.30	0.05		0.17	< 0.05	< 0.05	44.0	40.0	40.0	53	98	177		328	44.14	68.5%	
LTP 9	24.81	18.66	5.10	50.42	0.38	0.31	<0.05		0.17	0.15	< 0.05	43.0	23.9	38.8	59	115	193		367	43.47	68.1%	
LTP11	25.13	19.07	2.51	52.54	0.28	0.25	0.05		0.17	< 0.05	< 0.05	43.9	46.8	39.1	55	94	174		323	44.20	68.0%	
LTP16	31.83	12.27	3.39	51.59	0.26	0.42	0.06		0.17	< 0.05	< 0.05	44.1	49.1		79	76	200		355	44.11	66.1%	
LTP10	24.48	17.89	2.48	54.46	0.21	0.28	0.05		0.16	< 0.05	< 0.05	42.3	3.62	19.1	58	90	169		317	42.37	64.7%	
LTP 4	24.04	17.78	3.31	53.85	0.31	0.26	0.05		0.15	0.25	< 0.05	41.5	3.71	4.77	56	95	180		331	41.83	64.3%	
LTP 5	24.22	17.17	4.91	52.72	0.33	0.30	< 0.05		0.14	0.21	< 0.05	41.0	3.63	5.39	65	106	191		362	41.40	64.1%	
LTP17	38.39	5.54	3.41	51.22	0.40	0.42	0.07		0.16	0.38	< 0.05	43.6	45.2	43.8	83	32	191		306	43.94	63.9%	
LTP23	38.62	5.56	2.57	52.23	0.34	0.46	0.07		0.15	< 0.05	< 0.05	44.0	42.90		82	29	199		310	44.18	63.7%	
LTP14	30.93	11.01	4.90	51.96	0.30	0.45	0.05		0.15	0.25	< 0.05	41.8	3.24	3.92	78	69	191		338	41.95	63.0%	
LTP13	11.28	27.95	3.26	57.2	< 0.05	0.13	< 0.05		0.17	< 0.05	< 0.05	39.4	5.72	5.26	30	117	188		335	39.23	63.0%	
LTP12	30.93	11.35	3.36	53.52	0.32	0.31	0.06		0.15	< 0.05	< 0.05	42.0	2.55	30.1	82	72	207		361	42.27	62.6%	
LTP20	31.05	11.35	2.52	54.14	0.32	0.31	0.06		0.16	0.10	< 0.05	42.1	3.38	29.7	85	71	200		356	42.40	62.6%	
LTP15	36.89	5.70	5.05	51.22	0.31	0.43	0.10		0.16	0.13	< 0.05	42.5	3.41	5.03	88	35	204		327	42.59	62.2%	
LTP 3	22.89	16.69	6.70	52.58	0.25	0.29	< 0.05		0.14	0.46	< 0.05	39.4	23.3	29.5	43	166	141		350	39.58	61.9%	
LTP 7	10.37	27.85	3.29	58.18	< 0.05	0.15	< 0.05		0.16	< 0.05	< 0.05	38.4	10.9	15.5	36	132	152		320	38.23	61.4%	**A**
LTP52	24.9	11.5	4.89	54.8	2.06	0.28	0.05	<0.05	1.38	<0.05	<0.05	32.6	32.1		72	74	140		286	36.40	56.0%	
LTP51	28.7	11	1.62	56.6	1.38	0.29	0.07	<0.05	0.26	<0.05	<0.05	37.3	3.07	3.61	82	69	159		310	39.70	58.4%	**B**
LTP29	40.29	2.09	1.23	55.09	0.43	0.39	0.12		0.19	0.17	< 0.05	42.0	45.9		76	10	206		292	42.38	58.8%	
LTP21	36.62	5.58	2.54	54.19	0.39	0.46	0.07		0.15	< 0.05	< 0.05	42.0		35.5	58	34	208		300	42.20	60.3%	**C**
LTP30	39.40	1.96	2.22	55.25	0.45	0.41	0.10		0.21	<0.05	< 0.05	41.0	1.74	2.04	72	11	209		292	41.36	57.5%	
LTP41	31.36	9.48	0.85	55.63	0.27	0.30	0.07	1.88	0.16	<0.05	< 0.05	42.5	1.20	2.32	87	60	194	20	361	40.84	60.0%	
LTP 6	29.83	10.45	3.34	55.65	0.21	0.32	0.05		0.15	< 0.05	< 0.05	40.2	1.89	2.76	65	52	172		289	40.28	59.0%	
LTP34	30.44	9.81	1.68	57.3	0.25	0.31	0.07		0.15	<0.05	< 0.05	40.1	1.40	1.79	76	51	188		315	40.25	58.0%	
LTP43	30.51	9.68	1.68	56.19	0.28	0.32	0.07	1.11	0.15	<0.05	< 0.05	41.1	0.97	1.84	62	66	187	12	327	40.19	58.8%	
LTP42	30.55	9.56	0.86	57.13	0.27	0.33	0.07	1.08	0.15	<0.05	< 0.05	41.1	1.04	1.81	75	65	192	12	344	40.12	58.2%	
LTP47	22.2	17.4	3.98	55.2	0.31	0.31	0.05	<0.05	0.1	<0.05	<0.05	39.3	1.97	2.14	58	104	197		359	39.60	61.0%	
LTP38	34.82	4.73	0.82	57.84	0.31	0.30	0.08	0.94	0.15	<0.05	< 0.05	40.3	1.07	1.40	83	25	175	9	292	39.56	55.4%	
LTP 2	23.35	16.10	4.87	54.25	0.46	0.24	< 0.05		0.16	0.58	< 0.05	38.8	2.24	3.05	53	96	167		316	39.45	60.8%	
LTP39	34.35	4.73	1.67	57.39	0.27	0.30	0.08	1.06	0.14	<0.05	< 0.05	40.0	1.47	1.93	32	33	203	16	284	39.08	55.2%	
LTP 1	23.29	15.66	3.33	57.01	0.24	0.22	0.06		0.14	< 0.05	0.05	38.7	1.31	1.77	63	89	175		327	38.94	58.7%	
LTP48	32	6.87	7.8	52.4	0.52	0.34	0.05	<0.05	0.15	0.18	<0.05	38.2	1.24	1.53	84	48	205		337	38.87	57.7%	
LTP40	33.67	4.75	0.86	57.85	0.38	0.31	0.08	1.95	0.15	<0.05	< 0.05	40.0	1.15	2.39	40	32	194	25	291	38.42	54.5%	
LTP26	33.69	4.56	3.73	56.95	0.36	0.43	0.06		0.14	0.07	< 0.05	38.0	1.22	1.40	91	28	193		312	38.25	54.0%	
LTP27	28.91	9.33	3.66	57.32	0.22	0.36	0.05		0.14	<0.05	< 0.05	38.2	0.99	1.16	67	48	173		288	38.24	55.5%	
LTP46	28.4	8.69	2.67	59	0.29	0.33	0.06	<0.05	0.13	<0.05	<0.05	36.9	0.91	0.99	71	46	175		292	37.09	53.3%	

CLAIMS

1. The use of P_2O_5 as a component to improve the refractoriness of inorganic fibres comprising SiO_2, and CaO and/or MgO, to produce inorganic fibres having a composition such that the percentage of non-bridging oxygens is less than 61.4% and having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours.

2. Saline soluble inorganic fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, comprising:-

SiO_2	52 - <58wt% [52 - <58+0.5×(MgO-10)wt% if MgO > 10wt%]
CaO	22 - 40wt%
MgO	0 - 17.5wt%
MgO + CaO	< 42wt%
P_2O_5	0.5 - 10wt%
B_2O_3	0 - 2wt%

and in which the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is less than 61.4%.

3. Saline soluble inorganic fibres as claimed in claim 2 in which the fibres have a composition:-

SiO_2	52.4 - 57.85wt%
CaO	22.2 - 39.4wt%
MgO	1.96 - 17.4wt%
P_2O_5	0.82 - 7.8wt%
B_2O_3	0 - 1.95wt%
Al_2O_3	<1wt%

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